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The effect of structural parameters of the polycations

### ABSTRACT

The formation of polyelectrolyte complexes (PECs) between two complementary polyelectrolytes has been actively studied during the last three decades. The composition, structure and properties of the PECs are observed to have a strong dependence on the nature of the interacting polyelectrolytes. The present work is focussed on the effect of the structural parameters of the flexible, vinylic type polycations on their complexation behaviour with carboxymethylcellulose (CMC), a rigid polyanion.

Quaternized derivatives of poly(4-vinylpyridine), poly(2-vinylpyridine) and poly(4-vinylbenzylchloride) have been chosen as the polycations for the present study. The structural parameters of the polycations, viz., molecular weight, charge density, chemical and steric environment of the charged site etc. have been varied. The techniques of viscometry, conductometry and uv-vis spectrophotometry have been used to study the complexation behaviour of the systems selected and the nature of the resulting PECs.

The investigation of the complexing ability of the polycations towards complexation has been carried out making use of MO, an anionic dye molecule as a probe. The study of the metachromatic behaviour of the dye in the presence of the polycations shows the influence of the structural parameters on the nature of cooperative interactions that exists between oppositely charged polyelectrolytes. The contribution of coulombic and non-ionic forces on the cooperative interactions has been evaluated qualitatively.

The composition of the polycation-CMC complexes has been observed to be influenced by the charge density of the polycations in certain polyelectrolyte pairs. The effect is attributed to the difference in conformation of the two kinds of complexing polyions. Further, the possibility of formation of non-stoichiometric PECs in the soluble form has been observed to be governed by the nature of the polycations. Also, one of the properties of the PEC, the ability to transport low molecular weight solutes, in the membrane form, is correlated with the structure of the polycation.

The soluble PEC species has been investigated in detail to obtain information about the kinetics of its formation. The results are analysed on the basis of a theory applicable to the swelling of a gel network. It has been concluded that the swelling of the PEC network is a consequence of the reorganization of the ionic crosslinks in the PEC systems.